

Rare earth elements distribution in clay zones of sedimentary formation, Pondicherry, south India

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Abstract Concentrations of five rare earth elements (REE) were measured in clay samples of a deep bore hole comprising major aquifers of Pondicherry region, south India in order to investigate the geochemical variations among various litho-units. Clay samples from Cretaceous formation show distinct gray to black color whereas Tertiary deposits have clays with color varying from pale yellow to brown to gray. All measured REEs exhibit lower concentrations than Upper Continental Crust (UCC) average values. Large variations in REEs contents were observed in different sedimentary formations (Tertiary and Cretaceous). Chondrite normalized ratio of La/Lu and Eu/Eu* indicate that the clays are derived from weathering of felsic rock and possibly under humid climate. All the samples showed positive Eu anomaly in North American Shale Composite (NASC) normalized plot which shows plagioclase feldspar as the major

contributor to these clays. Positive Eu anomaly is also an indication of reduced condition of the formation.

Keywords REE distribution · Pondicherry · Sedimentary formation · Felsic rock · Weathering conditions

Introduction

Processes that produce sedimentary rocks include weathering, erosion, transportation-deposition and diagenesis. Elements (alkali and alkaline earth elements) with high solubility in natural waters have greater potential for being fractionated during sedimentary processes, in contrast a number of elements with low solubility in water provide strong estimates of the average composition of their source regions, which include Sc, Th, Y and rare earth elements (REE) [1].

Rare earth elements being immobile under surface conditions and resistant to diagenesis and metamorphism provide useful information on provenance [2–4], identification of source rock [5, 6] and understanding paleo-redox condition of the aquifers [7, 8]. Despite REE having similar chemical and physical properties because of their electronic configuration, fractionation is observed between light and heavy REE which is mainly due to different nature of the coordination complexes they form in rock forming minerals [9]. This behavior of REEs has been used by many researchers in understanding various petrological, mineralogical and sedimentation processes [10–13].

Initial studies on REE behavior during weathering of rocks showed that REEs are mobile and fractionate during weathering [12–14]. However, it was opined that sedimentary processes homogenize the REE fractionations that occurred during formation of igneous rocks and obscure the

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changes taking place during weathering and transportation. Recent studies showed that weathering of source rocks can also cause fractionation [15, 16].

The REE distribution in sediments of south India has been attempted by a few researchers [17–20]. Study carried out in flood plains of Cauvery basin established that weathered hornblende and titanite contribute to the sediments [17], and in sedimentary rocks of Bhima basin the source rock is found to be felsic igneous rocks [18]. Similarly studies carried out to identify the atmosphere prevailed during the formation of limestone in Kudankulam formation indicated oxygen rich environment [19]. In Silakkudi formation of Ariyalur group sandstones the major contribution was found to be from sediments originating from Dharwar craton [20].

The objective of the present paper is to evaluate the distribution of REE in clay zones of different sedimentary formations of Pondicherry region and to relate their systematics to interpret the nature of source rock and weathering conditions in respective formations. Clay samples were chosen for this study as they are widely used as environmental indicators of provenance studies, paleoredox conditions and stratigraphic correlations [21].

Materials and methods

Study site description

The entire area of Pondicherry region is covered by sedimentary formations ranging from Cretaceous to Recent ages with a patch of Charnokite formation belonging to Archean age in the northwestern part [22, 23]. The oldest sedimentary formations are the Cretaceous sediments of Mesozoic era and are further subdivided into four different formations. The Cretaceous formation is overlain by Tertiary sediments which are further sub divided into three different formations. Quaternary formations overlie the Tertiary deposits and are mostly alluvium and lateritic soil. This region is affected by the tectonic disturbances, because of which there is a large variation in the thickness and lateral extent of different formations. Sedimentation processes in this region were influenced by sea transgressions and regressions [24, 25] and also

by tectonic processes [26]. This region mainly depends on Cuddalore (Tertiary) and Vanur (Cretaceous) sedimentary aquifers for groundwater resources. The Quaternary alluvium formations are also being utilized for groundwater supply in few regions.

Collection of clay samples

The clay samples were collected from seven different depths (24–27, 33–36, 48–51, 57–60, 102–105, 126–129, 135–138 m below ground level) during drilling of a borehole in Andiarpalayam village located west of Pondicherry with geographical coordinates; 11°55′30″N latitude, 79°37′14″E longitude and topographic elevation of 15 m above mean sea level. Borehole cutting samples were collected at 3 m interval and based on the nature of the in situ sediments seven clay samples from depths given above were chosen for REE analysis. Four out of seven samples belong to Tertiary formation and rest Cretaceous formation.

Analytical methods

Fifty grams of the each clay sample was dried in an oven and carefully ground using mortar and agar from which 75 mg of the powdered sample was sealed doubly in aluminum foil and irradiated in self serve facility of CIRUS reactor, Mumbai with a neutron flux of $10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ for 6 h. The rare earth element (La, Ce, Eu, Yb and Lu) concentrations were determined using instrumental neutron activation analysis (INAA). IAEA RMs SL-1 and Soil-7 were used as reference and control standards, respectively. Gamma-ray measurements were carried out after appropriate cooling time by using Ge detector coupled with a computer assisted multichannel analyzer. The details of target nuclei, half life, gamma energies and measured values for different elements in IAEA RM soil-7 is shown in Table 1.

Results and discussion

Analytical results by INAA are given in Table 2. REE data of North American Shale Composite (NASC) [27], Post

Table 1 INAA data of the measured rare earth elements and measured values of IAEA RM Soil-7

S. No.	Radionuclide	Half life	Gamma energy (KeV)	Recommended values (mg kg ⁻¹)	This work (mg kg ⁻¹), ±1σ error	Detection limit (mg kg ⁻¹)
1	¹⁴⁰ La	40.3 h	487.03	28	29.3 ± 0.3	0.30
2	¹⁴¹ Ce	32.5 days	145.45	61	64.2 ± 1.6	2.34
3	¹⁵² Eu	13.5 years	344.3	1	1.10 ± 0.05	0.10
4	¹⁷⁵ Yb	4.2 days	396.32	2.4	2.34 ± 0.09	0.17
5	¹⁷⁷ Lu	6.7 days	208.36	0.3	0.33 ± 0.01	0.02

Table 2 REE data of the clay samples (mg kg⁻¹) and normalized ratios of Eu/Eu*, La/Lu

Depth	La	Ce	Eu	Yb	Lu	∑REE	(La/Lu) cn	(Eu/Eu*) cn	(Eu/Eu*)nasc
24–27 m	18.4 ± 0.2	31.9 ± 1.2	0.74 ± 0.05	0.61 ± 0.08	0.11 ± 0.01	51.66	17.90	0.47	1.89
33–36 m	18.5 ± 0.2	33.8 ± 1.3	0.91 ± 0.05	0.51 ± 0.08	0.13 ± 0.01	53.77	15.30	0.55	2.34
48–51 m	31.5 ± 0.3	58.8 ± 1.6	1.38 ± 0.07	1.67 ± 0.11	0.19 ± 0.02	93.51	16.78	0.46	1.66
57–60 m	10.3 ± 0.2	15.8 ± 1.0	0.66 ± 0.05	1.01 ± 0.08	0.11 ± 0.01	27.91	9.52	0.73	1.95
102–105 m	26.8 ± 0.1	49.9 ± 0.9	1.06 ± 0.03	1.16 ± 0.05	0.13 ± 0.01	79.10	21.16	0.42	1.61
126–129 m	19.9 ± 0.3	39.4 ± 1.5	0.59 ± 0.05	0.83 ± 0.09	0.14 ± 0.01	60.85	14.36	0.30	1.18
135–138 m	26.3 ± 0.2	50.3 ± 1.3	1.30 ± 0.05	1.40 ± 0.08	0.21 ± 0.01	79.47	13.15	0.51	1.84
Sandstone ^a	9.0 ± 0.2	16.6 ± 1.6	0.42 ± 0.06	0.41 ± 0.09	0.09 ± 0.01	26.56	10.12	0.51	1.89
NASC	32	73	1.24	3.1	0.48				
PAAS	38.2	79.6	1.08	2.82	0.43				
UCC	30	64	0.88	2.2	0.32				
Chondrite (CI) ^b	0.237	0.613	0.0563	0.161	0.0246				

Errors reported are due to counting statistics for single measurement

cn chondrite normalized; nasc NASC normalized; NASC composite 40 shales, mainly North American [27]; PAAS average 23 post-Archean shales from Australia [1]; UCC upper continental crust [1]

^a From the study area

^b Averages for Chondrite(CI) based on data of McDonough W. F. and Sun S. [31]

Archean Australian shales (PAAS) [1] and upper continental crust (UCC) [1] are also included in the table for comparison.

Litholog characterization

Cretaceous deposits are found below ~60 meters below ground level (m bgl) and their lithology down the depth changes from gray claystones, silts and fine grained calcareous sandstones to hard, coarse grained occasionally feldspathic or calcareous quartzite sandstones to black carbonaceous silty clays and fine to medium grained sands with bands of lignite and medium to coarse grained sandstones. Tertiary deposits were found between 15 and 60 m bgl with lithology varying from coarse grained sandstones with minor clays and siltstone to white to dirty white sandy, hard calcareous sandstone and clay. The top zone up to 15 m bgl is Quaternary formation mostly with lateritic soils and alluvium. Clay samples from Cretaceous formation show distinct gray to black color whereas Tertiary deposits have clays with color varying from pale yellow to brown to gray.

Vertical distribution of REE

The REE data is plotted against the depth shown in Fig. 1. The UCC value of the respective elements is also included to evaluate the relative enrichment or depletion in these clay samples. In general all the measured REEs show similar pattern. It can be seen that light REE (La and Ce) show higher concentrations compared to heavy REE (Yb and Lu). In comparison to the UCC values all the clay samples show depleted REE concentrations except Eu whose

concentrations fall close to UCC average concentration. This decrease in REE concentration compared to UCC could be due to contribution from biogenic carbonates with low REE content [15]. Clay samples collected from Tertiary formations show more variations compared to those collected from Cretaceous formation except for Ce and Eu.

REE systematics

REE behavior is assessed based on their normalized concentrations with respect to a chosen reference material. A plot of logarithm of the normalized abundance versus the element is commonly used to represent the REE data in graphical form. Normalization is carried out in order to smooth out large difference in concentrations between REEs which is due to odd–even effect. In most of the cases Chondrite is used for normalization, however NASC and PAAS are also used as references especially for sedimentary formations [1, 15].

Chondrite normalized rare earth element patterns are shown in Fig. 2. It is observed that light REE show significant enrichment compared to heavy REE which show a flat pattern. This could be due to fractionation of light REE over heavy REE. The REE patterns of these samples are inclined and mostly parallel to each other which is suggestive of similar source rocks.

In the case of NASC normalized REE patterns of the clay samples, it is observed that the curve is flat and show depletion in REE compared to UCC and PAAS as shown in Fig. 3. The plotted position for Eu was found to be lying away from the trend defined by the other REE which is termed as europium anomaly. In general the magnitude of

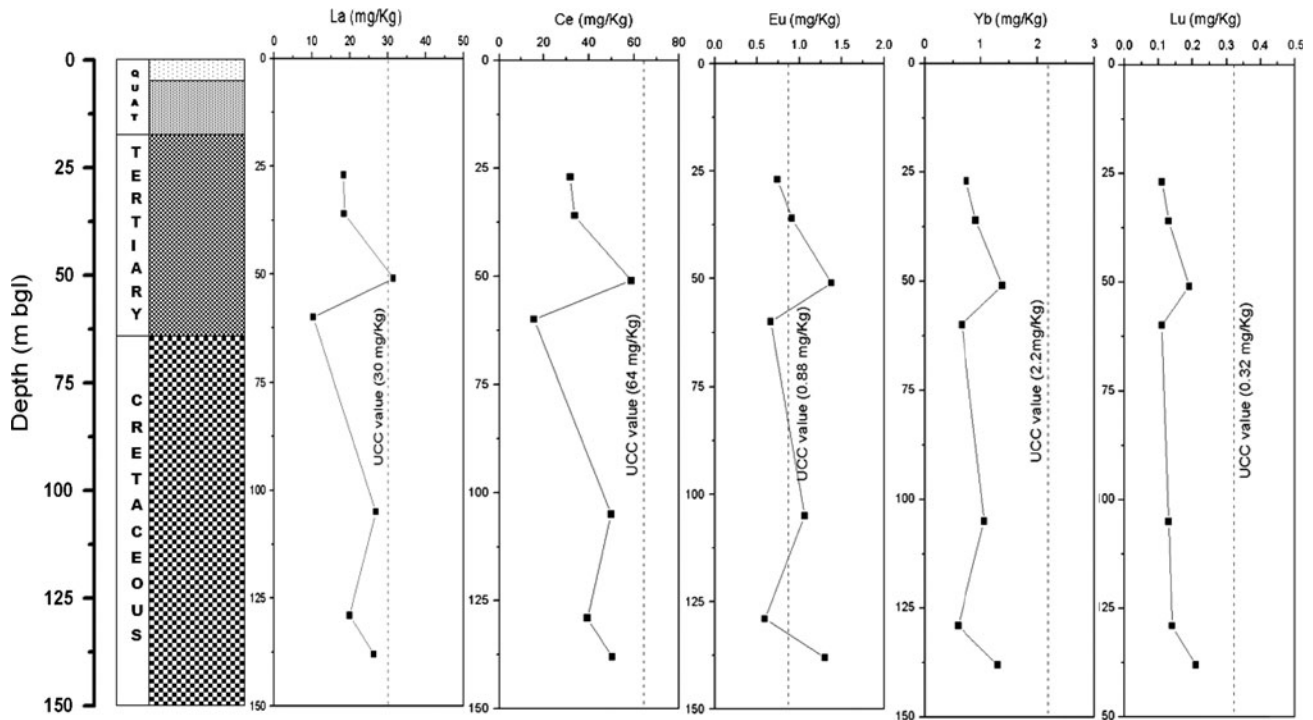


Fig. 1 Depth profiles of REE in different formations. Dashed lines indicate UCC value of respective REE

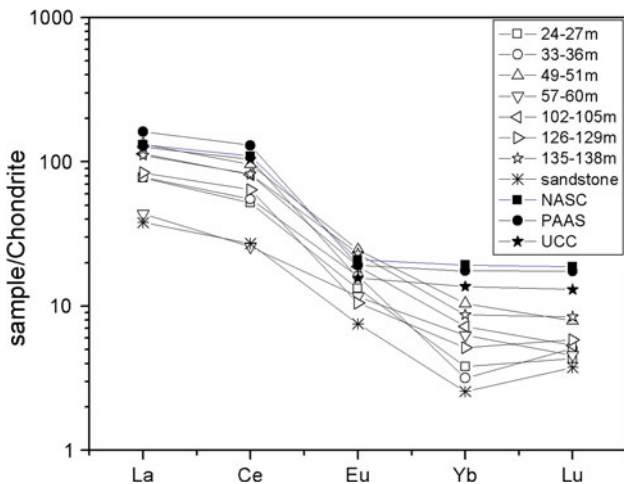


Fig. 2 Chondrite normalized REE pattern of the studied clays and sandstone. The plots of UCC, PAAS and NASC are shown for comparison

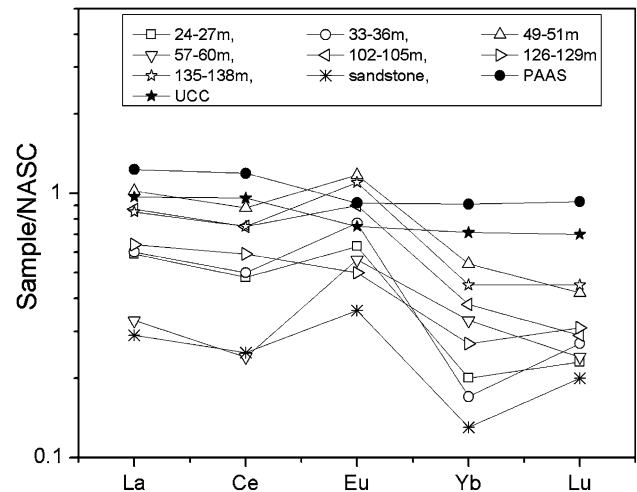


Fig. 3 NASC normalized REE pattern of the studied clays and sandstone. The plots of UCC and PAAS are shown for comparison

Eu anomaly is represented by Eu/Eu^* ratio, which is defined as the ratio of the calculated value of Eu (normalized value) and the predicted value of Eu^* obtained by interpolation from normalized values of adjacent REEs (Sm and Gd). However in the present paper Ce and Yb were used for interpolation therefore Eu/Eu^* values are approximate. The Eu/Eu^* ratios normalized with respect to Chondrite and NASC are given in Table 2.

This anomaly in Eu is due to its ability to form divalent cation. Under reducing conditions Eu^{3+} converts to Eu^{2+}

resulting in additional increase in ionic size of about 17% subsequently Eu^{2+} enters different silicate minerals than the other trivalent REE, becoming relatively enriched or depleted, resulting in anomalous REE distribution pattern [1]. As the ionic radii of Sr^{2+} and Eu^{2+} are similar, Eu becomes highly concentrated in the common mineral group of the plagioclase feldspars, in which Eu^{2+} along with Sr^{2+} enters the major Ca^{2+} sites. Therefore sediments/clays derived from plagioclase feldspars invariably show a pronounced positive Eu anomaly. In the present case all the

clay samples show a positive Eu anomaly indicating contribution of plagioclase feldspar. Positive Eu anomaly also indicates reducing conditions of the formation [28, 29]. Presence of lignite beds which are indicative of reducing condition in these formations supports this finding.

In the both the plots (Figs. 2 and 3) clay samples show higher REE contents compared to sandstone which is due to dilution effect by quartz [15]. It is shown that REEs are present mainly in clays and in whole rock they tend to decrease with increasing content of quartz. In order to verify the nature of source rock (felsic or mafic), chondrite normalized ratios of Eu/Eu* and La/Lu were compared with the source rock values (Table 3). From the table it can

Table 3 Range of elemental ratios in different source rocks, UCC and samples from study area (clays and sandstone)

Elemental Ratio	(Eu/Eu*) _{cn}	(La/Lu) _{cn}
Felsic source ^a	0.4–0.94	3.0–27.0
Mafic source ^a	0.71–0.95	1.1–7.0
UCC	0.63	9.73
Upper Cretaceous formation, Cauvery basin [20]	0.35–1.73	4.1–23.53
Clays ^b	0.3–0.73	9.5–21.2
Sandstone ^b	0.51	10.12

cn chondrite normalized

^a References [32–34]

^b This study

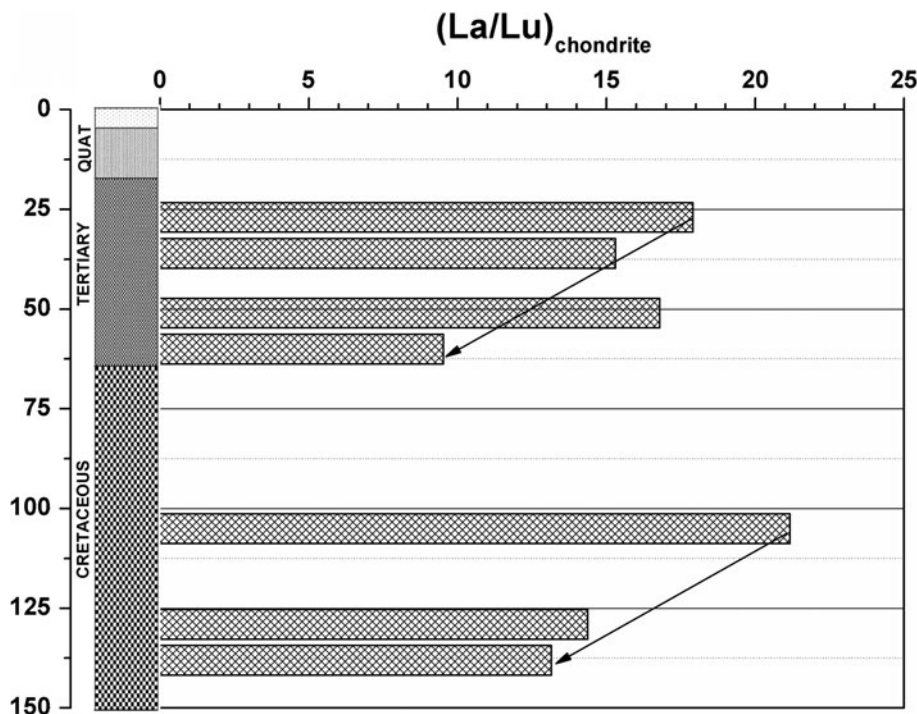
be found that the ratios for clay samples as well as sandstone fall within the range of felsic source rock. The ratios were also found to be similar to those of sediment samples analyzed from upper Cretaceous sedimentary formation in Ariyalur group located south of Pondicherry [20].

La/Lu normalized ratios

The fractionation of light REE from heavy REE can also be expressed in the form of a chondrite-normalized elemental ratio. This ratio gives a measure of the overall slope of the normalized plot and thereby extent of fractionation between light and heavy REE. In the study the fractionation between light and heavy REE was studied by considering the ratio of La (light REE) to Lu (heavy REE).

It is seen from the Fig. 4 that the normalized La/Lu ratios (9.5–22) vary down the depth. This enrichment of La over Lu can be explained by the preferential adsorption of La on clays or fine sediments present in the formation whereas Lu being a heavy element forms stable complexes in water leading to depletion in sediments. Similar observations were found by other researchers [7]. Although there is no clear distinction in La/Lu ratio of Cretaceous and Tertiary formations, there seems to be a general decrease in this ratio with depth in each formation. This can be attributed to the presence of low amount of heavy REE during later stages clay deposition compared to initial stages. Also the presence of other phases (coarse sand and limestone) might have altered this ratio which needs further study.

Fig. 4 Depth-wise variation of Chondrite normalized ratio of La/Lu. Solid line is trend line indicating decreasing La/Lu ratio within each formation



Presence of wide variation in La/Lu ratio (9.5–22) and in total measured REE contents (ΣREE : 28–93 mg kg⁻¹) indicate that the sedimentary formations could have formed under humid condition. Mobilization of REE under humid conditions causes intense chemical weathering leading to preferential transport of REE, especially heavy ones into the water and results in wide variation of light to heavy REE ratios [30]. This wide variation in La/Lu ratios also indicates significant post depositional changes.

Conclusions

The distribution of REEs was studied in clay samples of a borehole at Andiarpalayam comprising diverse sedimentary formations with different geological time scales. The clay samples were selected from Tertiary and Cretaceous formations which form major aquifers of this region. Chondrite normalized patterns of REE in the clay samples are mostly parallel with enriched light REEs compared to heavier ones. These patterns are suggestive of common source rock for these clays. NASC normalized REE pattern indicate a positive Eu anomaly (Eu/Eu* ratio: 1.2–2.3). This positive Eu anomaly reflects the contribution of plagioclase feldspar to these clays and also reducing condition of the formation. This observation is further supported by the presence of lignite and gray color of the clay which are indicative of deposition under reducing condition. The nature of source rock is verified using Chondrite normalized La/Lu and Eu/Eu* ratios. These ratios found to match with that of felsic rocks. High variability in measured total REEs and (La/Lu)_{cn} ratios point to weathering of the rocks under humid conditions.

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